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(54) OXIDE ELECTRODE THIN FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To improve residual polarization characteristics in a ferroelectric capacitor type memory using PZT or the like by a method which is comprised of epitaxially growing a ferroelectrics having a perovskite-type structure and an oxide lower electrode in the (100) or (001) direction on a (100) silicon substrate although it has been hitherto impossible to allow the perovskite-type oxide to orient in (100) or (001) direction on a (100) silicon substrate or on a (100) fluorite structure buffer layer.

SOLUTION: A ferroelectric capacitor of (100) or (001) orientation is realized by epitaxially growing an MO layer 3 (M=Ca, Sr, Ba) comprising an MO layer being part of the perovskite structure and having NaCl structure in the (100) direction on a (100) silicon substrate 1 or on a (100) fluorite structure buffer layer 2 and then successively depositing a perovskite oxide electrode thin film 4 such as SrRuO3, a ferroelectric layer 5 and an oxide electrode thin film 6.
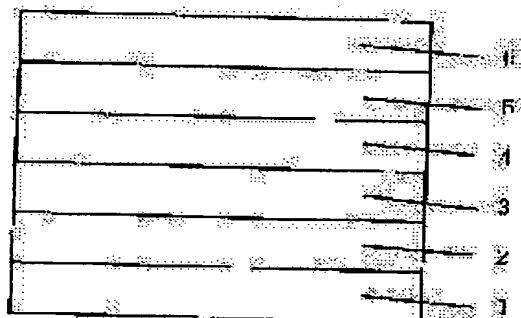
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(54)【発明の名称】　酸化物電極薄膜

(57)【要約】

【課題】　PZTなどを用いた強誘電体キャパシタ型メモリにおいて、残留分極特性を向上させるためには、（100）シリコン基板上にペロブスカイト構造を有する強誘電体および酸化物下電極を（100）あるいは（001）方向にエピタキシャル成長させる必要があるが、従来、（100）シリコン基板上あるいは（100）フルオライト構造バッファ層上に、ペロブスカイト酸化物を（100）あるいは（001）配向させることは不可能であった。

【解決手段】　（100）シリコン基板1上、あるいは（100）フルオライト構造バッファ層2上に、ペロブスカイト構造の一部であるMO層からなるNaCl構造のMO層3（M=Ca、Sr、Ba）を（100）方向でエピタキシャル成長させ、その後、$SrRuO_3$などのペロブスカイト酸化物電極薄膜4、強誘電体層5、酸化物電極薄膜6を堆積することにより、（100）あるいは（001）配向の強誘電体キャパシタを実現する。

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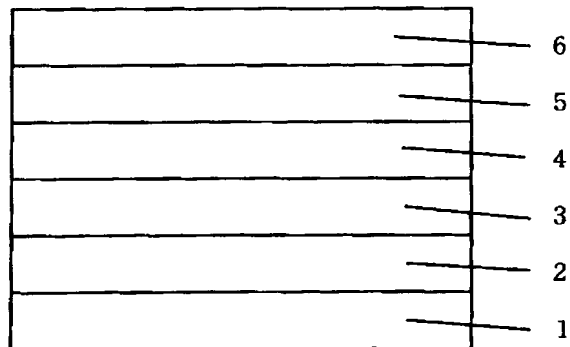
【特許請求の範囲】

【請求項１】　（１００）シリコン基板と、前記シリコン基板上に少なくともＮａＣｌ構造の（１００）配向した金属酸化物ＭＯ（Ｍ＝Ｃａ、Ｓｒ、Ｂａ）を含むバッファ層と、前記バッファ層上にペロブスカイト構造の擬立方晶で（１００）配向に相当する金属酸化物層ＡＢＯ$_3$とを有することを特徴とする酸化物電極薄膜。

【請求項２】　前記バッファ層は、フルオライト構造の（１００）配向した金属酸化物からなる第１バッファ層と、前記第１バッファ層上にＮａＣｌ構造の（１００）配向した金属酸化物ＭＯ（Ｍ＝Ｃａ、Ｓｒ、Ｂａ）からなる第２バッファ層とからなることを特徴とする請求項１記載の酸化物電極薄膜。

【請求項３】　前記第１バッファ層は、（１００）配向したイットリア安定化ジルコニアＺｒ$_{1-x}$Ｙ$_x$Ｏ$_{2-0.5x}$（０ｘ０．４５）と（１００）配向した酸化セリウムＣｅＯ$_2$からなることを特徴とする請求項２記載の酸化物電極薄膜。

【請求項４】　前記金属酸化物層ＡＢＯ$_3$は、ＭＲｕＯ$_3$（Ｍ＝Ｃａ、Ｓｒ、Ｂａ）からなることを特徴とする請求項１記載の酸化物電極薄膜。

【請求項５】　前記金属酸化物層ＡＢＯ$_3$は、Ｌａ$_{1-x}$Ｓｒ$_x$ＶＯ$_3$（０．２３ｘ１）からなることを特徴とする請求項１記載の酸化物電極薄膜。

【請求項６】　前記金属酸化物層ＡＢＯ$_3$は、Ｌａ$_{1-x}$Ｓｒ$_x$ＭｎＯ$_3$（０．２ｘ０．４）からなることを特徴とする請求項１記載の酸化物電極薄膜。

【請求項７】　前記金属酸化物層ＡＢＯ$_3$は、Ｌａ$_{1-x}$Ｓｒ$_x$ＣｏＯ$_3$（０．４ｘ０．６）からなることを特徴とする請求項１記載の酸化物電極薄膜。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、酸化物電極薄膜に関し、特に、この酸化物電極薄膜を用いた強誘電体メモリなどの酸化物デバイスに関する。

【０００２】

【従来の技術】近年、強誘電体を用いた不揮発性メモリの開発が急速に進展している。強誘電体としては、ＰｂＺｒ$_{1-x}$Ｔｉ$_x$Ｏ$_3$（ＰＺＴ）、Ｂａ$_{1-x}$Ｓｒ$_x$ＴｉＯ$_3$（ＢＳＴ）、ＳｒＢｉ$_2$Ｔａ$_2$Ｏ$_9$（ＳＢＴ）等の材料が注目されているが、中でも菱面体－正方晶相境界（ＭＰＢ）付近の組成のＰＺＴ材料が、その残留分極、抗電界特性に優れており、最も実用化の進展している材料である。

【０００３】強誘電体メモリは、強誘電体をキャパシタとして用い１Ｔ／１Ｃ構造などを形成する強誘電体キャパシタ型と、強誘電体をＳｉＯ$_2$の代わりにゲート絶縁膜として用いるＭＦＳＦＥＴ型とに分類される。１Ｔ／１Ｃ型の強誘電体キャパシタ構造においては、シリコン（Ｓｉ）などの基板上に電極層を形成し、その上に強誘電体層を形成することになるので、電極材料の選択が強

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誘電体の特性に大きな影響を与える。強誘電体キャパシタの電極材料として要求される特性は、

（１）電気抵抗が十分低い。

（２）強誘電体材料との格子定数のミスマッチが小さい。

（３）耐熱性が高い。

（４）反応性が低い。

（５）拡散バリア性が高い。

（６）基板、強誘電体との密着性が良い。

などである。

【０００４】従来、ＰＺＴ系強誘電体の電極材料として用いられてきたのはＰｔである。Ｐｔは最密充填構造である面心立方格子（ＦＣＣ）構造をとるため自己配向性が強く、ＳｉＯ$_2$のようなアモルファス上に成膜すると（１１１）に強く配向し、その上の強誘電体膜も配向性が良い。しかし、配向性が強いため柱状結晶が成長し、粒界に沿ってＰｂなどが下地に拡散しやすくなるといった問題があった。またＰｔとＳｉＯ$_2$との密着性にも問題があった。

【０００５】ここでＰｔとＳｉＯ$_2$との密着性の改善のためにＴｉ、さらにＰｂなどの拡散バリア層としてＴｉＮなどを用いても、複雑な電極構造になる上、Ｔｉの酸化、ＴｉのＰｔ中への拡散、それに伴うＰＺＴの結晶性の低下が起こり、Ｐ－Ｅヒステリシス特性、リーク電流特性、ファティーグ特性などの電気特性が劣化する。

【０００６】このようにＰｔ電極には多くの問題があるため、ＲｕＯ$_x$やＩｒＯ$_2$をはじめ、導電性酸化物電極材料が研究されている。中でも、ペロブスカイト構造を有するＳｒＲｕＯ$_3$は、ＰＺＴと同じ結晶構造を有しているので、界面での接合性に優れ、ＰＺＴのエピタキシャル成長を実現しやすく、Ｐｂの拡散バリア層としての特性にも優れている。従って、ＳｒＲｕＯ$_3$を電極として用いた強誘電体キャパシタの研究が盛んに行われている。

【０００７】

【発明が解決しようとする課題】しかし、ＳｒＲｕＯ$_3$電極を酸化物電極薄膜、ＰＺＴを強誘電体として強誘電体キャパシタを構築する場合、以下のような問題があった。

【０００８】ＰＺＴは、Ｚｒ：Ｔｉ＝０．４８：０．５２のＭＰＢよりＴｉ過剰側の例えばＺｒ：Ｔｉ＝０．３：０．７、０．２：０．８の組成が、残留分極Ｐ$_r$の増大、抗電界Ｅ$_c$の低減の点から重要である。またこの組成領域でのＰＺＴは正方晶を示し、その分極方向はｃ軸に平行である。従って、上部電極／強誘電体／下部電極／基板の構造を有する強誘電体キャパシタでは、強誘電体層ＰＺＴの（００１）配向膜を得るため、下部電極であるＳｒＲｕＯ$_3$電極自体を（１００）方向（擬立方晶）に配向成長させる必要がある。

【０００９】ところが、Ｓｉ上にペロブスカイト型酸化

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物であるＳｒＲｕＯ₃電極を直接エピタキシャル成長させることは、困難である。そこで、Ｓｉ上に何らかのバッファ層をエピタキシャル成長させ、その上にＳｒＲｕＯ₃電極をエピタキシャル成長させる必要がある。

【００１０】ここで、Ｓｉ上にペロブスカイトと類似の構造を有するＹＢａ₂Ｃｕ₃Ｏₓをエピタキシャル成長させるためのバッファ層としては、イットリア安定化ジルコニアＺｒ$_{1-x}$Ｙₓ$O_{2-0.5x}$（ＹＳＺ）、ＣｅＯ₂、Ｙ₂Ｏ₃などフルオライト構造を有する酸化物が用いられてきた。また、Ｙ₂Ｏ₃／ＹＳＺ（(1) Appl. Phys. Lett., 61 1240 (1992)）、ＣｅＯ₂／ＹＳＺ（(2) Appl. Phys. Lett., 64 1573 (1994)）の二重バッファ層もＹＢａ₂Ｃｕ₃Ｏₓをエピタキシャル成長させることが確かめられている。この場合ＹＢａ₂Ｃｕ₃Ｏₓは容易に（００１）配向する。

【００１１】ところが、単純ペロブスカイト構造であるＳｒＲｕＯ₃（擬立方晶においてａ＝０．３９３ｎｍ、$2^{1/2}$ａ＝０．５５６ｎｍ）の場合は、フルオライト型構造のＹＳＺ（ａ＝０．５１４ｎｍ）あるいはＣｅＯ₂（ａ＝０．５４１ｎｍ）の（１００）面上には、格子の不整合はＣｅＯ₂の場合で３％程度と小さいにも関わらず、（１００）方向にエピタキシャル成長しない。これは、（１００）配向のフルオライト構造においては、最表面がＣｅイオンのみまたは酸素イオンのみの電荷が中和されない面であるのに対し、（１００）配向のペロブスカイト型構造では、各ＡＯ、ＢＯ₂層ともに陽イオン、陰イオンからなる電荷の中和された面であり、下地の最表面と堆積層の第一層との静電相互作用によって、反発力が生ずるためである。

【００１２】例えば、（１００）ＹＳＺ基板上には（１１０）配向（擬立方晶）することが知られている（(3) Appl. Phys. Lett., 67 1387~1389 (1995)）。これは、（１００）配向のフルオライト構造の最表面に（１１０）配向のペロブスカイト構造が積層する場合、（１１０）面方向にＡＢＯ面、Ｏ₂面が積層する構造であり、各面の電荷が中和しておらず静電相互作用の観点で安定であるために、（１００）配向のフルオライト構造の上に容易に配向するものと考えられる。

【００１３】さらに、（１００）ＳｒＲｕＯ₃／（１００）ＣｅＯ₂／（１００）Ｓｉの酸化物積層構造および製造方法が提案されている（(4)特開平１０−１８２２９２）。しかしながら実際には（１００）ＣｅＯ₂／（１００）Ｓｉのエピタキシャル成長は、６００℃以上の高温かつ１０$^{-8}$Torr以下の高真空雰囲気下でしか可能でなく、しかも単一配向膜にはならず、（１１０）ＣｅＯ₂／（１００）Ｓｉの領域と共存する（(5)Jpn. J. Appl. Phys., 29, L1199 (1990)）。また（１００）ＳｒＲｕＯ₃／（１００）ＣｅＯ₂／（１００）ＹＳＺ／（１００）ＳｉのＳｒＲｕＯ₃にも（１１０）方向と（１００）方向とが共存している。

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【００１４】以上のように、ＳｒとＲｕが同時供給されて成長する限りは、Ｓｉ基板上あるいはフルオライト構造のバッファ層上に、（１００）配向のペロブスカイト構造ＳｒＲｕＯ₃は得られない。これは、ＳｒＲｕＯ₃のみならず、ＣａＲｕＯ₃、ＢａＲｕＯ₃、その他のペロブスカイト酸化物の場合でも同様である。

【００１５】そこで、本発明は、Ｓｉ基板上あるいはＳｉ基板上のフルオライト構造を有するバッファ層の上に、（１００）配向したペロブスカイト構造の酸化物電極薄膜を提供することを目的としている。

【００１６】
【課題を解決するための手段】請求項１記載の酸化物電極薄膜は、（１００）Ｓｉ基板と、前記Ｓｉ基板上に少なくともＮａＣｌ構造の（１００）配向した金属酸化物ＭＯ（Ｍ＝Ｃａ、Ｓｒ、Ｂａ）を含むバッファ層と、前記バッファ層上にペロブスカイト構造の擬立方晶で（１００）配向に相当する金属酸化物層ＡＢＯ₃とを有することを特徴とする。

【００１７】請求項２記載の酸化物電極薄膜は、フルオライト構造の（１００）配向した金属酸化物からなる第１バッファ層と、前記第１バッファ層上にＮａＣｌ構造の（１００）配向した金属酸化物ＭＯ（Ｍ＝Ｃａ、Ｓｒ、Ｂａ）からなる第２バッファ層とからなるバッファ層を有することを特徴とする。ただし、フルオライト構造の第１バッファ層は省略し、ＮａＣｌ構造のバッファ層だけにすることも可能である。

【００１８】請求項３記載の酸化物電極薄膜は、第１バッファ層において、（１００）配向したイットリア安定化ジルコニアＺｒ$_{1-x}$Ｙₓ$O_{2-0.5x}$（０ｘ０．４５）と（１００）配向した酸化セリウムＣｅＯ₂からなることを特徴とする。

【００１９】請求項４記載の酸化物電極薄膜は、金属酸化物層ＡＢＯ₃において、ＭＲｕＯ₃（Ｍ＝Ｃａ、Ｓｒ、Ｂａ）からなることを特徴とする。

【００２０】請求項５記載の酸化物電極薄膜は、金属酸化物層ＡＢＯ₃において、Ｌａ$_{1-x}$ＳｒₓVO_3（０．２３ｘ１）からなることを特徴とする。

【００２１】請求項６記載の酸化物電極薄膜は、金属酸化物層ＡＢＯ₃において、Ｌａ$_{1-x}$ＳｒₓMnO_3（０．２ｘ０．４）からなることを特徴とする。

【００２２】請求項７記載の酸化物電極薄膜は、金属酸化物層ＡＢＯ₃において、Ｌａ$_{1-x}$ＳｒₓCoO_3（０．４ｘ０．６）からなることを特徴とする。

【００２３】
【発明の実施の形態】以下、本発明の実施形態を図面に基づいて説明する。

【００２４】（実施例１）図１は本発明の酸化物電極薄膜の第１の実施例を示す図である。

【００２５】ＹＳＺターゲットを用いたレーザーアブレーション法により、基板温度７００℃、酸素分圧１×１

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0^{-6}Ｔｏｒｒの条件で、Ｓｉ基板１上にフルオライト構造のＹＳＺバッファ層２を５０ｎｍ堆積した。ただし、基板温度、酸素分圧は、これに限るものではない。

【００２６】次に、ＳｒＯターゲットを用いたレーザーアブレーション法により、基板温度７００℃、酸素分圧３ｍＴｏｒｒの条件で、ＮａＣｌ構造のＳｒＯバッファ層３を１０ｎｍ堆積した。ただし、基板温度、酸素分圧は、これに限るものではない。

【００２７】さらに、$SrRuO_3$ターゲットを用いたレーザーアブレーション法により、基板温度７００℃、酸素分圧３ｍＴｏｒｒの条件で、ペロブスカイト構造のＳｒＲｕＯ$_3$電極層４を５０ｎｍ堆積した。ただし、基板温度、酸素分圧は、これに限るものではない。

【００２８】その後、$PbZr_{0.5}Ti_{0.5}O_3$ターゲットを用いたレーザーアブレーション法により、基板温度７００℃、酸素分圧３ｍＴｏｒｒの条件で、ペロブスカイト構造の$PbZr_{0.5}Ti_{0.5}O_3$強誘電体層５を１００ｎｍ堆積した。ただし、基板温度、酸素分圧は、これに限るものではない。

【００２９】最後に、$SrRuO_3$ターゲットを用いたレーザーアブレーション法により、基板温度７００℃、酸素分圧３ｍＴｏｒｒの条件で、ペロブスカイト構造のＳｒＲｕＯ$_3$上電極層６を５０ｎｍ堆積した。ただし、基板温度、酸素分圧は、これに限るものではない。

【００３０】得られた薄膜キャパシタは、膜面に垂直方向で（１００）ＳｒＲｕＯ$_3$／（００１）ＰＺＴ／（１００）ＳｒＲｕＯ$_3$／（１００）ＳｒＯ／（１００）ＹＳＺ／（１００）Ｓｉ、面内で［１１０］ＳｒＲｕＯ$_3$／／［１１０］ＰＺＴ／／［１１０］ＳｒＲｕＯ$_3$／／［１００］ＳｒＯ／／［１００］ＹＳＺ／／［１００］Ｓｉであった。

【００３１】上電極表面での電気抵抗率を４端子法によって測定したところ、＝２００μｃｍの値が得られ、５０Ｋから室温までの広い温度範囲にわたって金属的な温度依存性を示した。

【００３２】得られた強誘電体キャパシタについて、周波数１ｋＨｚ、振幅１００ｋＶ／ｃｍの電界を印加してヒステリシス測定を行った結果、$P_r＝50C/cm^2$、$E_c＝30kV/cm$の特性が得られ、分極反転10^{12}回までファティーグによるP_rの劣化は起こらなかった。これは、（１００）Ｓｉ基板上に（１００）ＹＳＺバッファ層を介してエピタキシャル成長させた（１１０）ＰＺＴ薄膜を有する強誘電体キャパシタの場合の$P_r＝30C/cm^2$、$E_c＝50kV/cm$、ファティーグ特性10^{11}回と比較して、強誘電体メモリとしてのより高い電気特性を有している。

【００３３】上述のように、フルオライト構造のＹＳＺおよびＮａＣｌ構造のＳｒＯからなる二重バッファ層を用いてＳｉ基板上に（１００）配向ペロブスカイト酸化物電極薄膜を堆積することにより、強誘電体キャパシタ

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のP_r、E_c、ファティーグ特性を向上させることが可能となる。

【００３４】（実施例２）図２は本発明の酸化物電極薄膜の第２の実施例を示す図である。

【００３５】ＳｒＯターゲットを用いたレーザーアブレーション法により、基板温度７００℃、酸素分圧$1×10^{-6}$Ｔｏｒｒの条件で、Ｓｉ基板上２１上にＮａＣｌ構造のＳｒＯバッファ層２２を１０ｎｍ堆積した。ただし、基板温度、酸素分圧は、これに限るものではない。

【００３６】さらに、$La_{0.7}Sr_{0.3}MnO_3$ターゲットを用いたレーザーアブレーション法により、基板温度７００℃、酸素分圧３ｍＴｏｒｒの条件で、ペロブスカイト構造の$La_{0.7}Sr_{0.3}MnO_3$下電極層２３を５０ｎｍ堆積した。ただし、基板温度、酸素分圧は、これに限るものではない。

【００３７】その後、$PbZr_{0.5}Ti_{0.5}O_3$ターゲットを用いたレーザーアブレーション法により、基板温度７００℃、酸素分圧３ｍＴｏｒｒの条件で、ペロブスカイト構造の$PbZr_{0.5}Ti_{0.5}O_3$強誘電体層２４を１００ｎｍ堆積した。ただし、基板温度、酸素分圧は、これに限るものではない。

【００３８】最後に、$La_{0.7}Sr_{0.3}MnO_3$ターゲットを用いたレーザーアブレーション法により、基板温度７００℃、酸素分圧３ｍＴｏｒｒの条件で、ペロブスカイト構造の$La_{0.7}Sr_{0.3}MnO_3$上電極層２５を５０ｎｍ堆積した。ただし、基板温度、酸素分圧は、これに限るものではない。

【００３９】得られた薄膜キャパシタは、膜面に垂直方向で（１００）$La_{0.7}Sr_{0.3}MnO_3$／（００１）ＰＺＴ／（１００）$La_{0.7}Sr_{0.3}MnO_3$／（１００）ＳｒＯ／（１００）ＹＳＺ／（１００）Ｓｉ、面内で［１１０］$La_{1-x}Sr_xMnO_3$／／［１１０］ＰＺＴ／／［１１０］$La_{1-x}Sr_xMnO_3$／／［１００］ＳｒＯ／／［１００］ＹＳＺ／／［１００］Ｓｉであった。

【００４０】ここで$La_{1-x}Sr_xMnO_3$においてｘ＝０．３としたが、０．２ｘ０．４であれば、同様の効果が得られる。

【００４１】得られた強誘電体キャパシタについて、周波数１ｋＨｚ、振幅１００ｋＶ／ｃｍの電界を印加してヒステリシス測定を行った結果、$P_r＝45C/cm^2$、$E_c＝30kV/cm$の高い電気特性が得られ、分極反転10^{12}回までファティーグによるP_rの劣化は起こらなかった。これは、（１００）Ｓｉ基板上に直接堆積させたＰＺＴ多結晶薄膜を有する強誘電体キャパシタの場合の$P_r＝10C/cm^2$、$E_c＝100kV/cm$、ファティーグ特性10^8回と比較して、強誘電体メモリとしてのより高い電気特性を有している。

【００４２】また、$La_{1-x}Sr_xMnO_3$の代わりに$La_{1-x}Sr_xVO_3$（０．２３ｘ１）、$La_{1-x}Sr_xCo$

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O_3（０.４ｘ０.６）を電極薄膜に用いた場合も同様の効果が得られる。

【００４３】上述のように、ＮａＣｌ構造のＳｒＯバッファ層を用いてＳｉ基板上に（１００）配向ペロブスカイト酸化物電極薄膜を堆積することにより、強誘電体キャパシタのP_r、E_c、ファティーグ特性を向上させることが可能となる。

【００４４】

【発明の効果】以上述べたように、本発明の酸化物電極薄膜によれば、シリコン基板上に、少なくとも最上面にＮａＣｌ構造を有するバッファ層を形成することにより、そのバッファ層上にペロブスカイト構造の酸化物電極薄膜を（１００）あるいは（００１）配向で成長させることができ、誘電体キャパシタメモリ、強誘電体キャパシタメモリ、ＭＦＳＦＥＴなどの電子デバイスを最適な構造で実現することができる。

【図面の簡単な説明】

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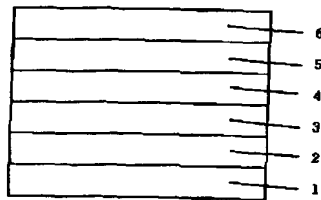
【図１】　本発明の一実施例を示すＳｒＲｕO_3酸化物電極薄膜を含んだ強誘電体キャパシタの断面図である。

【図２】　本発明の一実施例を示すＬａ$_{0.7}$Ｓｒ$_{0.3}$ＭｎO_3酸化物電極薄膜を含んだ強誘電体キャパシタの断面図である。

【符号の説明】
１．Ｓｉ基板
２．ＹＳＺバッファ層
３．ＳｒＯバッファ層
４．ＳｒＲｕO_3下電極層
５．ＰＺＴ強誘電体層
６．ＳｒＲｕO_3上電極層
２１．Ｓｉ基板
２２．ＳｒＯバッファ層
２３．Ｌａ$_{0.7}$Ｓｒ$_{0.3}$ＭｎO_3下電極層
２４．ＰＺＴ強誘電体層
２５．Ｌａ$_{0.7}$Ｓｒ$_{0.3}$ＭｎO_3上電極層

【図１】
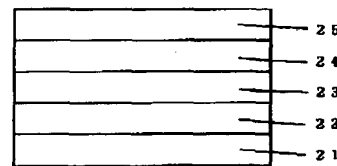
【図２】

* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] (100) The oxide electrode thin film characterized by having a silicon substrate, a buffer layer containing the metallic oxide MO (M=calcium, Sr, Ba) in which NaCl structure carried out orientation (100) at least on the aforementioned silicon substrate, and the metallic-oxide layer ABO3 that is equivalent to orientation (100) by the pseudo-cubic of a perovskite structure on the aforementioned buffer layer.
[Claim 2] The aforementioned buffer layer is an oxide electrode thin film according to claim 1 characterized by the bird clapper from the 1st buffer layer which consists of a metallic oxide in which fluorite structure carried out orientation (100), and the 2nd buffer layer which consists of a metallic oxide MO (M=calcium, Sr, Ba) in which NaCl structure carried out orientation (100) on the 1st buffer layer of the above.
[Claim 3] The 1st buffer layer of the above is an oxide electrode thin film according to claim 2 characterized by the bird clapper from the cerium oxide CeO2 which carried out orientation (100) to yttria-stabilized-zirconia Zr1-xYxO2-0.5x (0x0.45) which carried out orientation (100).
[Claim 4] The aforementioned metallic-oxide layer ABO3 is an oxide electrode thin film according to claim 1 characterized by the bird clapper from MRuO3 (M=calcium, Sr, Ba).
[Claim 5] The aforementioned account metallic-oxide layer ABO3 is an oxide electrode thin film according to claim 1 characterized by the bird clapper from La1-xSrxVO3 (0.23x1).
[Claim 6] The aforementioned metallic-oxide layer ABO3 is an oxide electrode thin film according to claim 1 characterized by the bird clapper from La1-xSrxMnO3 (0.2x0.4).
[Claim 7] The aforementioned account metallic-oxide layer ABO3 is an oxide electrode thin film according to claim 1 characterized by the bird clapper from La1-xSrxCoO3 (0.4x0.6).

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] Especially this invention relates to oxide devices, such as ferroelectric random-access memory using this oxide electrode thin film, about an oxide electrode thin film.
[0002]
[Description of the Prior Art] In recent years, development of the non-volatile memory using the ferroelectric is progressing quickly. As a ferroelectric, although material, such as $PbZr_{1-x}Ti_xO_3$ (PZT), $Ba_{1-x}Sr_xTiO_3$ (BST), and $SrBi_2Ta_2O_9$ (SBT), attracts attention, it is the material to which the PZT material of composition near a rhombohedron-tetragonal phase boundary (MPB) is excellent in the remanence and the anti-electric-field property, and utilization is progressing most especially.
[0003] Ferroelectric random-access memory is classified into the ferroelectric capacitor type which forms 1T / 1C structure, using a ferroelectric as a capacitor, and the MFSFET type which uses a ferroelectric as a gate insulator layer instead of SiO_2. In the ferroelectric capacitor structure of 1T/1C type, since an electrode layer will be formed on substrates, such as silicon (Si), and a ferroelectric layer will be formed on it, selection of an electrode material has big influence on the property of a ferroelectric. For the property demanded as an electrode material of a ferroelectric capacitor, (1) electric resistance is a low enough.
(2) The mismatch of a lattice constant with ferroelectric material is small.
(3) Thermal resistance is high.
(4) Reactivity is a low.
(5) Diffusion barrier property is high.
(6) Adhesion with a substrate and a ferroelectric is good.
It is ****.
[0004] Conventionally, Pt has been used as an electrode material of a PZT system ferroelectric. If a self-stacking tendency is strong and forms membranes on [like SiO_2] amorphous in order to take the face-centered cubic lattice (FCC) structure which is a close packed structure (111), orientation of the Pt will be carried out strongly, and the ferroelectric film on it also has a good stacking tendency. However, since the stacking tendency was strong, the columnar crystal grew, and there was a problem of becoming easy to diffuse Pb etc. on a ground along with a grain boundary. Moreover, there was a problem also in the adhesion of Pt and SiO_2.
[0005] For an improvement of the adhesion of Pt and SiO_2, Ti and when [even if it uses TiN etc. as diffusion barrier layers, such as Pb further,] becoming complicated electrode structure, oxidization of Ti, diffusion into Pt of Ti, and the crystalline fall of PZT accompanying it take place here, and electrical properties, such as an P-E hysteresis characteristic, a leakage-current property, and a fatigue property, deteriorate.
[0006] Thus, since there are many problems in Pt electrode, RuOx and IrO_2 are begun and the conductive oxide electrode material is studied. Especially, since it has the same crystal structure as PZT,

SrRuO3 which has a perovskite structure is excellent in the junction nature in an interface, tends to realize epitaxial growth of PZT and is excellent also in the property as a diffusion barrier layer of Pb. Therefore, research of the ferroelectric capacitor using SrRuO3 as an electrode is done briskly.

[0007]
[Problem(s) to be Solved by the Invention] However, when a ferroelectric capacitor was built by using PZT as a ferroelectric, having used SrRuO3 electrode as the oxide electrode thin film, there were the following problems.

[0008] Composition of the overTi side, Zr:Ti=0.3:0.7 [for example,], and 0.2:0.8 is more important for PZT than MPB of Zr:Ti=0.48:0.52 from increase of Remanence Pr, and the point of reduction of the anti-electric field Ec. Moreover, PZT in this composition field shows a tetragonal phase, and the direction of polarization is parallel to c axis. Therefore, in order to obtain the orientation (001) film of the ferroelectric layer PZT, it is necessary to make a direction (100) (pseudo-cubic) carry out orientation growth of the SrRuO3 electrode itself which is a lower electrode in the ferroelectric capacitor which has the structure of an up electrode / ferroelectric / lower electrode / substrate.

[0009] However, it is difficult to grow epitaxially directly SrRuO3 electrode which is a perovskite type oxide on Si. Then, it is necessary to grow a certain buffer layer epitaxially on Si, and to grow SrRuO3 electrode epitaxially on it.

[0010] Here, as a buffer layer for growing epitaxially YBa2Cu3Ox which has perovskite and analogous structure, the oxide which has fluorite structures, such as yttria-stabilized-zirconia Zr1-xYxO2-0.5x (YSZ), CeO2, and Y2O3, has been used on Si. Moreover, it is confirmed that Y2O3/the double-buffers layer of CeO2 [YSZ ((1) Appl.Phys.Lett. and 61 1240 (1992)) and]/YSZ ((2) Appl.Phys.Lett. and 64 1573 (1994)) also grows YBa2Cu3Ox epitaxially. In this case, orientation of the YBa2Cu3Ox is carried out easily (001).

[0011] However, in SrRuO3 (it sets to a pseudo-cubic and is a= 0.556nm 21/2 a= 0.393nm) which is simple perovskite structure, on YSZ (a= 0.514nm) of fluorite type structure, or the field (100) of CeO2 (a= 0.541nm), although the mismatching of a grid is as small as about 3% at the case of CeO2, it does not grow epitaxially in a direction (100). this is a field where the charge of only oxygen ion is not neutralized [Ce ion] for the maximum front face in the fluorite structure of orientation (100) -- receiving -- the perovskite-type structure of orientation (100) -- every -- it is the field where the charge which AO and BO two-layer become from a cation and an anion was neutralized, and is for repulsive force to arise by the electrostatic interaction of the maximum front face of a ground, and the first pass of a deposit

[0012] For example, on the YSZ (100) substrate, carrying out orientation (pseudo-cubic) (110) is known ((3) Appl.Phys.Lett. and 67 1387-1389 (1995)). When the perovskite structure of orientation (110) carries out a laminating to the maximum front face of the fluorite structure of orientation (100), this is structure in which an ABO side and O2 page carry out a laminating in the direction of a field (110), and the charge of each side does not neutralize but it is considered to carry out orientation easily on the fluorite structure of orientation (100) in the viewpoint of an electrostatic interaction, since it is stable.

[0013] Furthermore, the oxide laminated structure and the manufacture method of SrRuO (100)3 / (100) CeO2/(100) Si are proposed ((4) JP,10-182292,A). However, in fact, epitaxial growth of CeO (100)2/ (100) Si is possible only under the elevated temperature of 600 degrees C or more, and the high-vacuum atmosphere of 10 to 8 or less Torrs, and moreover does not become a single orientation film, but coexists with the field of CeO (110)2/(100) Si ((5) Jpn.J.Appl.Phys., 29, and L1199 (1990)). Moreover (100), the direction (110) and the direction (100) live together also in SrRuO3 of SrRuO3/(100) CeO2/ (100) YSZ/(100)Si.

[0014] As mentioned above, as long as simultaneous supply of Sr and the Ru is carried out and they grow, the perovskite structure SrRuO3 of orientation (100) is not obtained on Si substrate or the buffer layer of fluorite structure. This is the same not only at SrRuO3 but the case of CaRuO3, BaRuO3, and other perovskite oxides.

[0015] Then, this invention aims at offering the oxide electrode thin film of the perovskite structure which carried out orientation (100) on the buffer layer which has the fluorite structure on Si substrate or

Si substrate.
[0016]
[Means for Solving the Problem] An oxide electrode thin film according to claim 1 is characterized by having Si (100) substrate, a buffer layer containing the metallic oxide MO (M=calcium, Sr, Ba) in which NaCl structure carried out orientation (100) at least on the aforementioned Si substrate, and the metallic-oxide layer ABO3 that is equivalent to orientation (100) by the pseudo-cubic of a perovskite structure on the aforementioned buffer layer.

[0017] An oxide electrode thin film according to claim 2 is characterized by having the buffer layer which consists of the 1st buffer layer which consists of a metallic oxide in which fluorite structure carried out orientation (100), and the 2nd buffer layer which consists of a metallic oxide MO (M=calcium, Sr, Ba) in which NaCl structure carried out orientation (100) on the 1st buffer layer of the above. However, it is also possible for the 1st buffer layer of fluorite structure to omit and to make it only the buffer layer of NaCl structure.

[0018] An oxide electrode thin film according to claim 3 is characterized by the bird clapper in the 1st buffer layer from the cerium oxide CeO2 which carried out orientation (100) to yttria-stabilized-zirconia Zr1-xYxO2-0.5x (0x0.45) which carried out orientation (100).

[0019] An oxide electrode thin film according to claim 4 is characterized by the bird clapper from MRuO3 (M=calcium, Sr, Ba) in the metallic-oxide layer ABO3.

[0020] An oxide electrode thin film according to claim 5 is characterized by the bird clapper from La1-xSrxVO3 (0.23x1) in the metallic-oxide layer ABO3.

[0021] An oxide electrode thin film according to claim 6 is characterized by the bird clapper from La1-xSrxMnO3 (0.2x0.4) in the metallic-oxide layer ABO3.

[0022] An oxide electrode thin film according to claim 7 is characterized by the bird clapper from La1-xSrxCoO3 (0.4x0.6) in the metallic-oxide layer ABO3.

[0023]
[Embodiments of the Invention] Hereafter, the operation gestalt of this invention is explained based on a drawing.

[0024] (Example 1) Drawing 1 is drawing showing the 1st example of the oxide electrode thin film of this invention.

[0025] By the laser ablation method using the YSZ target, 50nm of YSZ buffer layers 2 of fluorite structure was deposited on the Si substrate 1 on condition that substrate temperature [of 700 degrees C], and oxygen tension 1x10-6Torr. However, substrate temperature and oxygen tension are not restricted to this.

[0026] Next, 10nm of SrO buffer layers 3 of NaCl structure was deposited by the laser ablation method using the SrO target on condition that the substrate temperature of 700 degrees C, and oxygen tension 3mTorr. However, substrate temperature and oxygen tension are not restricted to this.

[0027] Furthermore, 50nm of SrRuO3 electrode layers 4 of a perovskite structure was deposited by the laser ablation method using SrRuO3 target on condition that the substrate temperature of 700 degrees C, and oxygen tension 3mTorr. However, substrate temperature and oxygen tension are not restricted to this.

[0028] Then, 100nm of 0.5O3 or so PbZr0.5Ti dielectric layers 5 of a perovskite structure was deposited by the laser ablation method using 0.5OPbZr0.5Ti3 target on condition that the substrate temperature of 700 degrees C, and oxygen tension 3mTorr. However, substrate temperature and oxygen tension are not restricted to this.

[0029] Finally, 50nm of SrRuO3 top electrode layers 6 of a perovskite structure was deposited by the laser ablation method for having used SrRuO3 target on condition that the substrate temperature of 700 degrees C, and oxygen tension 3mTorr. However, substrate temperature and oxygen tension are not restricted to this.

[0030] The obtained thin film capacitor was perpendicular to the film surface, and were SrO//[100] YSZ//[[110] PZT / [110] SrRuO3/////[110] SrRuO3// [100]] [100]Si in SrRuO(100)3/(001) PZT/(100) SrRuO3/(100) SrO/(100) YSZ/(100)Si, and the field.

[0031] When the electrical resistivity in an upper electrode front face was measured by 4 terminal method, the value of =200microcm was acquired and the temperature dependence like a metal was shown over the latus temperature requirement from 50K to a room temperature.

[0032] As a result of impressing the electric field of the frequency of 1kHz, and amplitude 100 kV/cm and performing hysteresis measurement about the obtained ferroelectric capacitor, the property (Pr=50 C/cm2 and Ec=30kV/cm) was acquired, and degradation of Pr by the fatigue did not take place to 1012 polarization reversal. This has the higher electrical property as ferroelectric random-access memory as compared with Pr=30 C/cm2 in the case of the ferroelectric capacitor which has the PZT (110) thin film grown epitaxially through the YSZ (100) buffer layer on Si (100) substrate, Ec=50 kV/cm, and 1011 fatigue properties.

[0033] As mentioned above, it becomes possible to raise Pr of a ferroelectric capacitor, Ec, and a fatigue property by depositing an orientation (100) perovskite oxide electrode thin film on Si substrate using the double-buffers layer which consists of YSZ of fluorite structure, and SrO of NaCl structure.

[0034] (Example 2) Drawing 2 is drawing showing the 2nd example of the oxide electrode thin film of this invention.

[0035] By the laser ablation method using the SrO target, 10nm of SrO buffer layers 22 of NaCl structure was deposited on Si substrate top 21 on condition that substrate temperature [of 700 degrees C], and oxygen tension 1x10-6Torr. However, substrate temperature and oxygen tension are not restricted to this.

[0036] Furthermore, 50nm of bottom electrode layers 23 of La0.7Sr0.3MnO3 of a perovskite structure was deposited by the laser ablation method using La0.7Sr0.3MnO3 target on condition that the substrate temperature of 700 degrees C, and oxygen tension 3mTorr. However, substrate temperature and oxygen tension are not restricted to this.

[0037] Then, 100nm of 0.5O3 or so PbZr0.5Ti dielectric layers 24 of a perovskite structure was deposited by the laser ablation method using 0.5OPbZr0.5Ti3 target on condition that the substrate temperature of 700 degrees C, and oxygen tension 3mTorr. However, substrate temperature and oxygen tension are not restricted to this.

[0038] Finally, 50nm of La0.7Sr0.3MnO3 top electrode layers 25 of a perovskite structure was deposited by the laser ablation method for having used La0.7Sr0.3MnO3 target on condition that the substrate temperature of 700 degrees C, and oxygen tension 3mTorr. However, substrate temperature and oxygen tension are not restricted to this.

[0039] The obtained thin film capacitor is perpendicular to a film surface. La(100)0.7Sr0.3MnO3/(001) PZT/(100) La0.7Sr0.3MnO3/(100) SrO/(100) YSZ/(100)Si, They were SrO//[100] YSZ//[[110] PZT / [110] La1-xSrxMnO3/////[110] La1-xSrxMnO3// [100]] [100]Si in the field.

[0040] Although referred to as x= 0.3 in La1-xSrxMnO3 here, the same effect will be acquired if it is 0.2x0.4.

[0041] As a result of impressing electric field with a frequency [of 1kHz], and an amplitude of 100kV [/cm] and performing hysteresis measurement about the obtained ferroelectric capacitor, the high electrical property of Pr=45 C/cm2 and Ec=30 kV/cm was acquired, and degradation of Pr by the fatigue did not take place to 1012 polarization reversal. This has the higher electrical property as ferroelectric random-access memory as compared with Pr=10 C/cm2 in the case of the ferroelectric capacitor which has the PZT polycrystal thin film made to deposit directly on Si (100) substrate, Ec=100 kV/cm, and 108 fatigue properties.

[0042] Moreover, the same effect is acquired when La1-xSrxVO3 (0.23x1) and La1-xSrxCoO3 (0.4x0.6) are used for an electrode thin film instead of La1-xSrxMnO3.

[0043] As mentioned above, it becomes possible by depositing an orientation (100) perovskite oxide electrode thin film on Si substrate using the SrO buffer layer of NaCl structure to raise Pr of a ferroelectric capacitor, Ec, and a fatigue property.

[0044]

[Effect of the Invention] forming at least the buffer layer which was described above and which has NaCl structure in the best side on a silicon substrate like according to the oxide electrode thin film of

this invention -- the buffer-layer top -- the oxide electrode thin film of a perovskite structure -- or (100) (001) it can be made to be able to grow up by orientation and electron devices, such as dielectric capacitor memory, ferroelectric capacitor memory, and MFSFET, can be realized with the optimal structure

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[Translation done.]

PRIOR ART

[Description of the Prior Art] In recent years, development of the non-volatile memory using the ferroelectric is progressing quickly. As a ferroelectric, although material, such as $PbZr_{1-x}Ti_xO_3$ (PZT), $Ba_{1-x}Sr_xTiO_3$ (BST), and $SrBi_2Ta_2O_9$ (SBT), attracts attention, it is the material to which the PZT material of composition near a rhombohedron-tetragonal phase boundary (MPB) is excellent in the remanence and the anti-electric-field property, and utilization is progressing most especially.
[0003] Ferroelectric random-access memory is classified into the ferroelectric capacitor type which forms 1T / 1C structure, using a ferroelectric as a capacitor, and the MFSFET type which uses a ferroelectric as a gate insulator layer instead of SiO_2. In the ferroelectric capacitor structure of 1T/1C type, since an electrode layer will be formed on substrates, such as silicon (Si), and a ferroelectric layer will be formed on it, selection of an electrode material has big influence on the property of a ferroelectric. For the property demanded as an electrode material of a ferroelectric capacitor, (1) electric resistance is a low enough.
(2) The mismatch of a lattice constant with ferroelectric material is small.
(3) Thermal resistance is high.
(4) Reactivity is a low.
(5) Diffusion barrier property is high.
(6) Adhesion with a substrate and a ferroelectric is good.
It is ****.
[0004] Conventionally, Pt has been used as an electrode material of a PZT system ferroelectric. If a self-stacking tendency is strong and forms membranes on [like SiO_2] amorphous in order to take the face-centered cubic lattice (FCC) structure which is a close packed structure (111), orientation of the Pt will be carried out strongly, and the ferroelectric film on it also has a good stacking tendency. However, since the stacking tendency was strong, the columnar crystal grew, and there was a problem of becoming easy to diffuse Pb etc. on a ground along with a grain boundary. Moreover, there was a problem also in the adhesion of Pt and SiO_2.
[0005] For an improvement of the adhesion of Pt and SiO_2, Ti and when [even if it uses TiN etc. as diffusion barrier layers, such as Pb further,] becoming complicated electrode structure, oxidization of Ti, diffusion into Pt of Ti, and the crystalline fall of PZT accompanying it take place here, and electrical properties, such as an P-E hysteresis characteristic, a leakage-current property, and a fatigue property, deteriorate.
[0006] Thus, since there are many problems in Pt electrode, RuOx and IrO_2 are begun and the conductive oxide electrode material is studied. Especially, since it has the same crystal structure as PZT, $SrRuO_3$ which has a perovskite structure is excellent in the junction nature in an interface, tends to realize epitaxial growth of PZT and is excellent also in the property as a diffusion barrier layer of Pb. Therefore, research of the ferroelectric capacitor using $SrRuO_3$ as an electrode is done briskly.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the cross section of the ferroelectric capacitor containing the SrRuO teroxide electrode thin film which shows one example of this invention.
[Drawing 2] It is the cross section of the ferroelectric capacitor containing the La0.7Sr0.3MnO teroxide electrode thin film which shows one example of this invention.
[Description of Notations]
1. Si Substrate
2. YSZ Buffer Layer
3. SrO Buffer Layer
4. Bottom Electrode Layer of SrRuO3
5. PZT Ferroelectric Layer
6. SrRuO3 Top Electrode Layer
21. Si Substrate
22. SrO Buffer Layer
23. Bottom Electrode Layer of La0.7Sr0.3MnO3
24. PZT Ferroelectric Layer
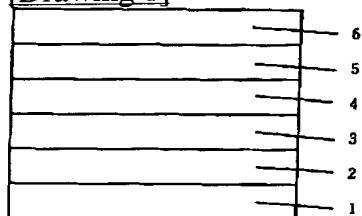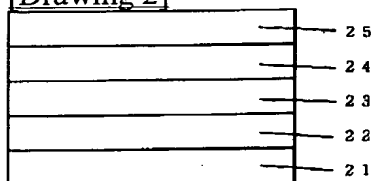25. La0.7Sr0.3MnO3 Top Electrode Layer

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DRAWINGS

[Drawing 1]

[Drawing 2]

[Translation done.]